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### Chapter One

#### BOTANOCHEMICALS\*

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#### INTRODUCTION

Energy-rich plant products useful as substitutes, supplements or complements of petrochemicals are now generally called botanochemicals (a term coined by the USDA public information officer, Dean Mayberry). Botanochemicals include substances which can be extracted directly from plants (primary botanochemicals) and those made by conversion of insoluble saccharides or lignocelluloses (secondary or derived botanochemicals). Primary botanochemicals include products such as naval stores (pine chemicals), tall-oil products (paper-pulping byproducts), oils for industrial uses, waxes, tannins, rubber, and gutta percha. Traditional secondary botanochemicals include

\* The mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.

furfural and ethanol. Potential new botanochemicals include latex- or whole-plant oils, guayule rubber, grass gutta, polyphenols, specialty seed oils, and such potential lignocellulose conversion products as methane, fuel alcohol, and various other fermentation-produced fuels and chemical intermediates.

Now that the price of petrochemicals has increased faster than the price of equivalent agricultural and forestry products, the latter have become more attractive. Various major U.S. petrochemical companies have recently announced that they are going to make substantial investments in new technologies for producing pine chemicals, guayule rubber, fuel alcohol from cellulosic residues, whole-plant oils, and other botanochemicals. Thus, the petrochemical industry appears already to have begun a shift toward a renewable resource base. Undue delay or failure to make this shift could eventually result in a "Kondratiev wave" economic recession.<sup>7</sup>

It is especially attractive from both social and economic viewpoints to consider adaptive agricultural systems<sup>12</sup> for integrated production of primary and secondary botanochemicals, protein feeds, and fibers. Such systems have been designated "multi-use botanochemical systems"; a scenario was presented for their introduction into U.S. agriculture<sup>4</sup> and economic and feasibility assessments were made.<sup>5</sup> Such systems can potentially make farm production of fuels and industrial feedstocks practical without necessarily decreasing the capacity for food production.

This review surveys and discusses in a cursive way botanochemical products from multi-use systems. Although integrated production schemes may be applicable to specialty crops for oilseeds, essential oils, botanicals, plant fibers, and vegetable dyestuffs, the discussion here relates to crops designed primarily for extraction of energy-rich basic feedstocks, that is, oils and hydrocarbons.

## BOTANO-CHEMICAL PRODUCTION

### Systems

Multi-use botanochemical systems offer major advantages

over other biomass utilization schemes (Figure 1). Greater economy and higher efficiency can be achieved by codevelopment of new crops and new handling, processing, and marketing systems than can be achieved just by making better use of residues from conventional crops. Expensive chemical conversion of plant products can be minimized by developing crops specially adapted to the system and capable of directly producing valuable energy-rich feedstocks. Leafy residues remaining after extraction of the energy-rich materials contain most of the plant protein and carbohydrates for feeds and foods, whereas woody stem residues are especially attractive as lignocellulose sources for conversion to fuel alcohol. Thus, multi-use botanocemical crop systems can make possible the agricultural production of fuels and industrial feedstocks without necessarily decreasing food production.

Figure 1 portrays only one optional system; crops and processing can be varied to provide a range of primary products. In secondary processing of woody residues, other fermentation products can be produced besides, or in addition to, ethanol. Also, instead of saccharification followed by fermentation, alternative processing can provide such products as solid fuel pellets, fiber and board products, cattle feeds, furfural, process gas, methanol, methane, or even liquid hydrocarbon fuels.

Crops. The U.S. Congress has already selected guayule (Parthenium argentatum) for development as the crop for domestic production of natural rubber.<sup>20</sup>

A screening program has so far resulted in identification of more than 40 plant species having some potential as new botanocemical crops.<sup>2-4</sup> Plant scientists and agronomists are now studying genetics, reproduction, and propagation of some of these candidates to select species for crop development. Assuming development of appropriate germplasm and cultural protocol, specifications for practical botanocemical crops have been proposed.<sup>5</sup> Table 1 compares the proposed crop specifications with typical compositions and estimated yields of wild plants, but does not imply that the new crops will necessarily be developed from the species used for comparison.

In Table 1, botanocemical crops are broadly classified

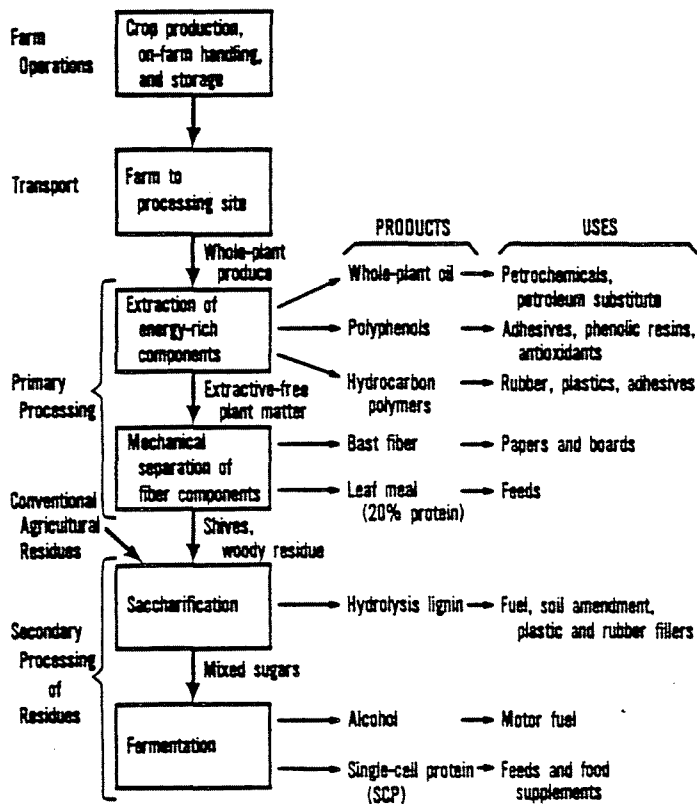


Fig. 1. Multi-use botanochemical systems.

TABLE 1  
Comparison of Botanochemical Crop Specifications with Estimated  
Yields and Typical Compositions of Wild Species<sup>a</sup>

Component	Herbaceous perennial oil crop <sup>b</sup> <u>Asclepias syriaca</u>		New crop specification		Woody perennial oil-polyphenol crop <sup>c</sup> <u>Rhus glabra</u>		New crop specification		Perennial grass gutta crop <sup>d</sup> <u>Elymus canadensis</u>		New crop specification	
	Composi- tion, %	Yield, kg/ha/ yr	Composi- tion, %	Yield, kg/ha/ yr	Composi- tion, %	Yield, kg/ha/ yr	Composi- tion, %	Yield, kg/ha/ yr	Composi- tion, %	Yield, kg/ha/ hr	Composi- tion, %	Yield, kg/ha/ yr
Total dry matter	100	12000	100	18000	100	8900	100	11500	100	11200	100	12500
Crude protein <sup>e</sup>	(11.1)	(1332)	(9)	(1620)	(6.7)	(596)	(6)	(690)	(17.2)	(1926)	(10)	(1250)
Gutta	---	---	---	---	---	---	---	---	1.9	213	12	1500
Whole-plant oil	7.6 <sup>f</sup>	912	14 <sup>f</sup>	2520	5.7	507	10	1150	2.8	314	8	1000
Polyphenol	7.2	864	7	1260	18.8	1673	18	2070	6.6	739	7	875
Leaf meal (20% protein) <sup>e</sup>	16.0	1920	32	5760	10.0	890	10	1150	---	---	---	---
Bast fiber	11.0	1320	6	1080	---	---	---	---	---	---	---	---
Residue <sup>e</sup>	58.2	6984	41	7830	65.5	5830	62	7130	88.7	9934	73	9125

<sup>a</sup> Yields and compositions are given on a dry weight basis.

<sup>b</sup> The new crop specification based on harvesting two crops of leafy plant per season. The Asclepias syriaca comparative data is for mature plants harvested in early September, dry yield estimated from individual plant weights and extrapolating to 107,600 plants per hectare.

<sup>c</sup> Woody plants handled as a coppice crop; harvested by cutting at near ground level, on a 2-year rotation. Dry yield for Rhus glabra estimated.

<sup>d</sup> Dry matter yields estimated on the basis of one cutting of mature plants per season. The Elymus canadensis data is from an unreplicated small cultivated plot harvested before full maturity.

<sup>e</sup> Crude protein is not extracted from the plant matter.

<sup>f</sup> This whole-plant oil contains about 20% low-molecular-weight natural rubber as a hydrocarbon component.

into three types, but actually the primary products will differ with species. The detailed composition of whole-plant oils and polyphenols is highly species-dependent. However, petroleum refinery processes may be insensitive enough to handle whole-plant oils without regard to crop species.<sup>8,19</sup> Thus, crop species may be important if chemical intermediates are being produced but noncritical for production of fuels, solvents, monomers, carbon black, and other basic chemicals.

Whole-Plant Oils. Whole-plant oils can potentially become major industrial feedstocks. They are like petroleum and the current commercial plant-derived feedstocks, naval stores, and tall oil, in that their composition is very complex. They are much more complex than industrial vegetable oils consisting mainly of triglycerides from seed or other plant storage organs. Whole-plant oils generally contain an entire spectrum of polar to nonpolar lipids (Figure 2). Their detailed composition depends not only on the plant species but also on the maturity of the plant and the method of extraction.<sup>3</sup>

Extraction and partitioning procedures can be varied to produce, from a given plant sample, oils containing the different proportions of polar and nonpolar components desired for different applications. For example, many temperate zone plants contain low-molecular-weight rubber<sup>17</sup> that may either be isolated and used as a polymer or be left as a hydrocarbon component of the oil.

Only a few whole-plant oils have been characterized in detail, but lipid classes have been estimated by thin-layer chromatography (TLC) for a defined oil-fraction from several productive species (Table 2). A distinctive feature of most whole-plant oils is their high content of waxy, nonglyceride esters that are less polar than triglycerides. Frequently, there are two distinct classes of nonglyceride esters, probably aliphatic wax esters and triterpenol esters (Figure 2 and Table 2).

Thus, whole-plant oils are valuable mixtures from which a wide variety of chemical intermediates including sterols, long-chain alcohols, rosin and fatty acids, esters, waxes, terpenes, and other hydrocarbons could be obtained. However, the cost of separation is likely to be high.

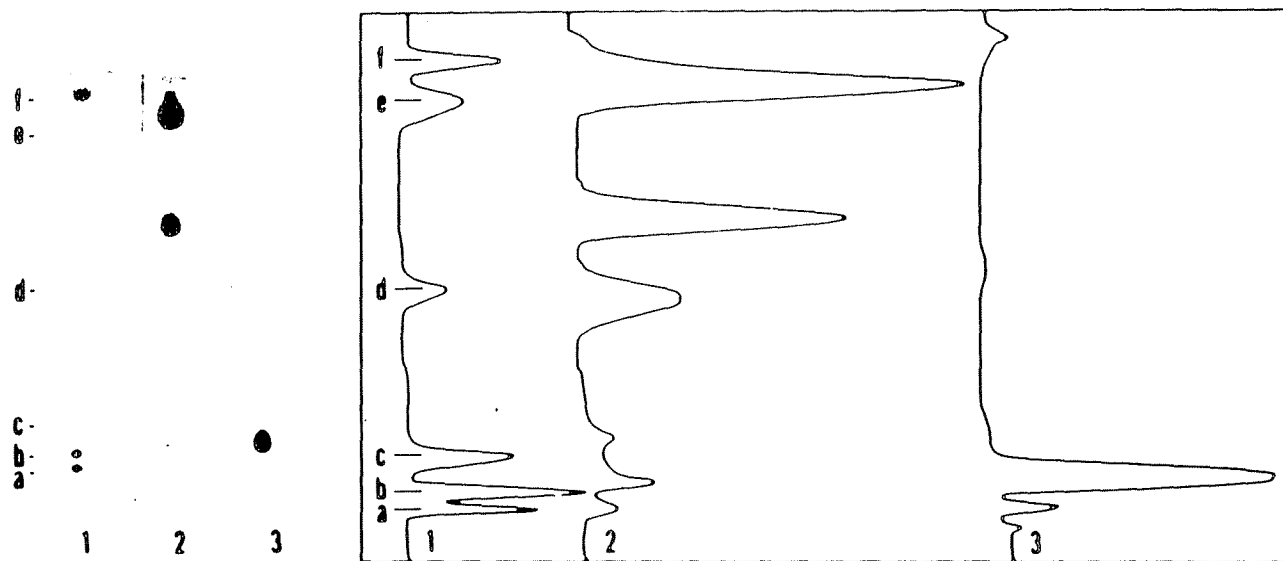


Fig. 2 Thin-layer chromatography of a representative whole-plant oil. Lane 1: mixed standard containing (a) sitosterol,  $R_f$  0.09; (b) oleyl alcohol,  $R_f$  0.12; (c) oleic acid,  $R_f$  0.18; (d) triolein,  $R_f$  0.47; (e) oleyl laurate,  $R_f$  0.80; and (f) squalene,  $R_f$  0.87. Lane 2: *Cirsium discolor* oil. Lane 3: *Cirsium discolor* unsaponifiable matter. The densitometer traces are for the corresponding TLC Lanes with migration distance expanded 1/25 times.

TABLE 2  
Lipid Classes in Whole-Plant Oils, Estimated by Thin-Layer Chromatography  
Oil Composition

Plant source	Harvest date	Oil content, %	Sterols, %	Other free alcohols, %	Free acids, %	Triglycerides, %	Nonglyceride esters, %	Hydrocarbons, %
<u>Ambrosia trifida</u>	9/20/77	4.21	11	4	7	68	7	3
<u>Asclepias incarnata</u>	7/28/77	2.70	9	15	8	13	48 <sup>a</sup>	7
<u>Asclepias syriaca</u>	7/27/77	4.46	5	11	5	trace	72 <sup>a</sup>	7
<u>Cacalia atriplicifolia</u>	8/3/77	2.99	10	24 <sup>b</sup>	7	10	43	6
<u>Campanula americana</u>	9/8/77	6.51	13	5	10	58	10	4
<u>Cirsium discolor</u>	10/5/77	5.66	2	4	4	21	67 <sup>a</sup>	2
<u>Eupatorium altissima</u>	9/20/77	6.08	6	5	7	36	44 <sup>a</sup>	2
<u>Euphorbia dentata</u>	8/25/77	4.13	6	6	5	42	36 <sup>a</sup>	5
<u>Euphorbia Lathyrus</u>	3/25/77	9.21	3	20	18	3 <sup>c</sup>	49	7
<u>Parthenium argentatum</u>	5/13/77	4.04	10	7	5	23	31 <sup>a</sup>	24
<u>Rhus glabra</u>	8/18/77	5.10	12	11	19	13	39	6
<u>Sassafras albidum</u>	9/8/77	2.26	8	46 <sup>b</sup>	--	2	28	16
<u>Sonchus arvensis</u>	6/10/77	4.63	5	19	5	5	60 <sup>a</sup>	6
<u>Vernonia altissima</u>	5/23/77	2.62	13	12	2	4	68 <sup>a</sup>	1

<sup>a</sup> Prominent nonglyceride ester spot at RF 0.6 in addition to the one at RF 0.8.

<sup>b</sup> Prominent spot taken as free alcohol at RF 0.23.

<sup>c</sup> Small spot at RF 0.46 is unsaponifiable.

Accordingly, a likely strategy is to employ crude separations to obtain marketable fractions for various end-uses (Figure 3). Alternatively, the whole-plant oil can be used as a feedstock for a petroleum refinery by employing appropriate process modifications.<sup>8,19</sup> As indicated in Figure 3, whole-plant oils would be unusually versatile feedstocks for production of the entire range of petrochemicals as well as tall oil, naval store, and inedible fat products.

## POLYPHENOLS

Although "polyphenols" is actually a generic term referring to a large complex of phytochemicals with hydroxy-substituted aromatic rings, we customarily use the term for crude plant extractives that are at least sparingly soluble in acetone and freely soluble in 87.5% aqueous ethanol (Figure 4). If anhydrous methanol or ethanol is used as the extraction solvent, larger yields of polyphenols of different composition are obtained as illustrated by Asclepias syriaca (Figure 5). All these crude products contain, in addition to actual polyphenols, a wide variety of complex lipids and other substances. For plants of high tannin content the polyphenol fraction might equally well be called a tannin extract (note Rhus glabra in Table 1). Acetone-extracted polyphenol fractions contain 52-60% carbon and have higher heating values than methanol but considerably lower than whole-plant oils.

Commercial tannins and bark extractives from tree species used for lumber and pulpwood have been studied with a view toward expanded industrial utilization<sup>9,15</sup> (Figure 6). Tannin-based plywood adhesives and water-treatment compounds are commercial products in South Africa. A polyphenol fraction from creosote bush is used as antioxidant for guayule rubber in Mexico. About 30 million kg/yr of vegetable tanning materials is imported into the U.S. However, most of the uses for polyphenols indicated in Figure 6 are only potential.

If large volumes of low-cost plant polyphenols became available, they could become very important chemical feedstocks. However, polyphenol fractions that are likely products from botanocchemical processing have not been

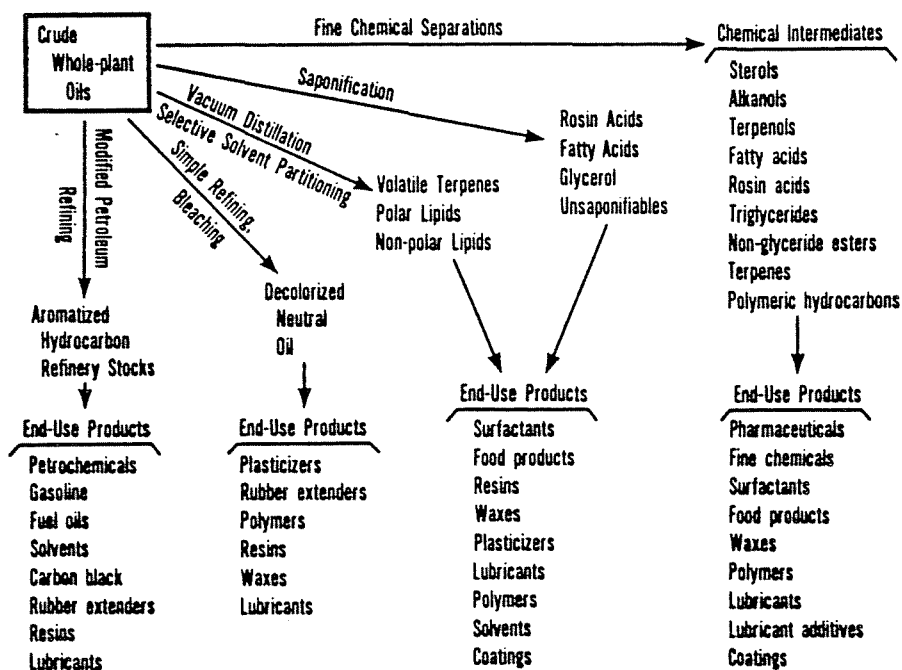


Fig. 3 Strategies for industrial utilization of whole-plant oils

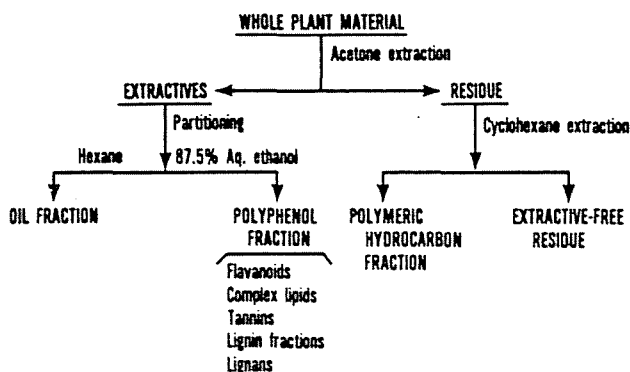


Fig. 4 Separation of crude polyphenol fraction from plant materials

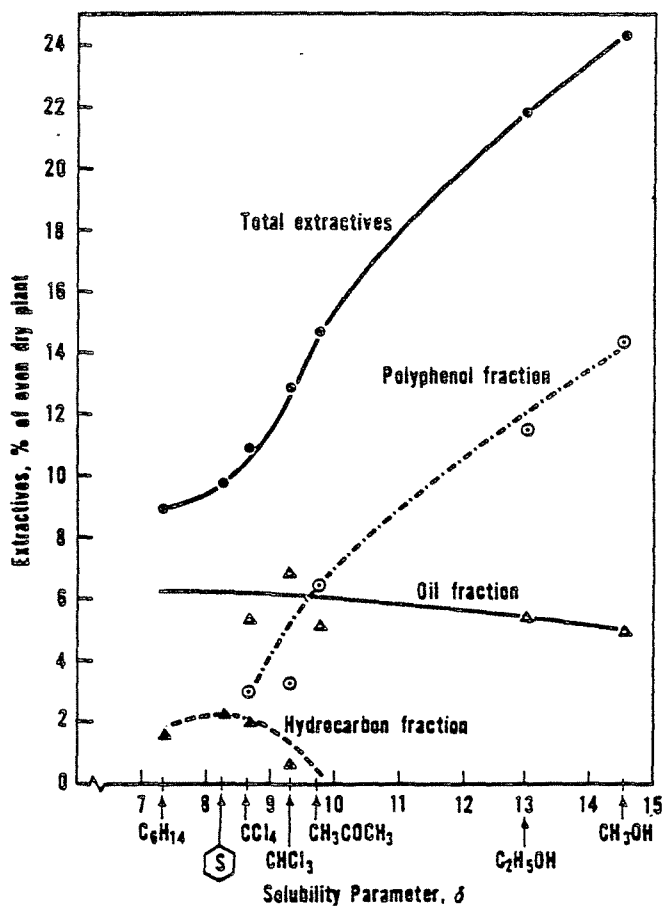


Fig. 5 Yield of polyphenol fraction as a function of solvent type. Exhaustive Soxhlet extraction of Ascepias syriaca.

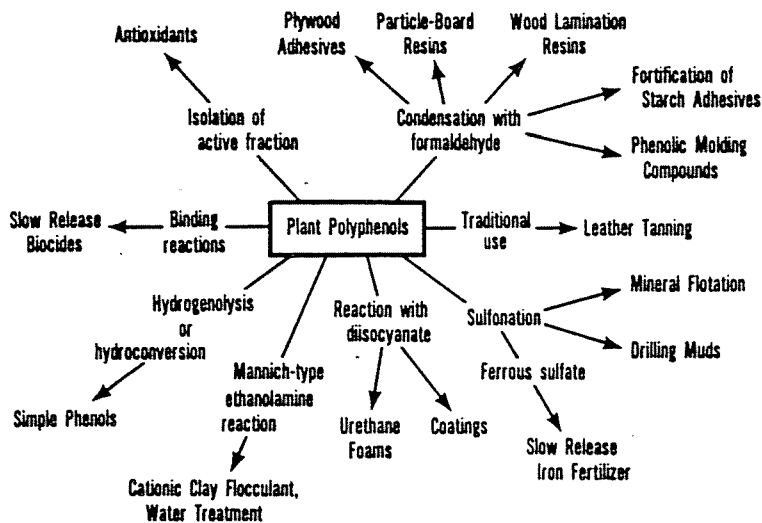


Fig. 6 Routes to industrial utilization of crude plant polyphenols

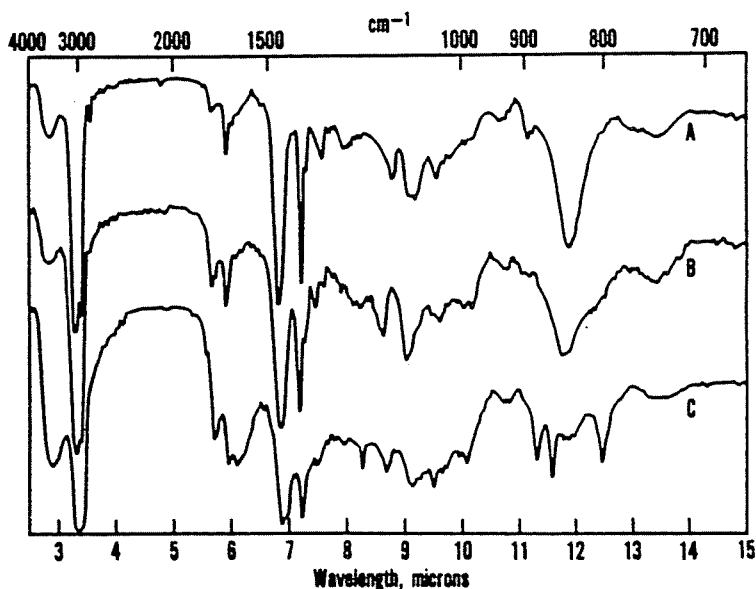


Fig. 7 Infrared spectra. A--natural rubber from *Monarda didyma*. B--amorphous gutta from *Elymus canadensis*. C--crystalline gutta from *Elymus canadensis*

characterized. Their composition is species dependent so that product and market development can only begin after the new crop species have been selected. Possibly, conversion to simple phenols would be less sensitive to feedstock variations than alternative routes to utilization (Figure 6).

#### HYDROCARBON POLYMERS

cis-1,4-Polyisoprene (natural rubber, NR) is the most common hydrocarbon polymer found in green plants. Since the U.S. is now committed to producing NR for polymer uses from guayule, other crops are less likely to be developed specifically for high-molecular-weight rubber.

Most of the plant species identified to produce NR contain less than 1%, dry whole-plant basis, of polymer that is too low in molecular weight<sup>1</sup> for conventional mixing and processing (Table 3). Low-molecular-weight natural rubbers would be of interest as a plasticizing additive (processing aid) to rubber mixes, for liquid rubber processing methods, for making cements (adhesives), and if low enough in cost as hydrocarbon feedstocks.

It would not be necessary to separate low-molecular-weight rubber from whole-plant oils intended for use as a petroleum refinery feedstock. Thus, perhaps the plant breeder's goal should be to develop crop varieties high in total content of oil plus low-molecular-weight polyisoprenes.

A few species of grasses may be potential sources of gutta (trans-1,4-polyisoprene<sup>6</sup>) (Table 4). Known species contain less than 2% gutta, dry whole-plant basis. Although the molecular weights of grass guttas are lower than those of most commercially important natural rubbers, they are high enough for the more crystalline polymer to have useful properties.<sup>10</sup> Gutta could have large-scale applications as both a thermoplastic and a thermosetting resin if it were available at prices competitive with NR and synthetic polymers.

In analytical screening of plants, infrared spectroscopy (IR) is relied on for routine detection of isoprene

TABLE 3  
Weight Average Molecular Weight ( $\bar{M}_w$  and Molecular Weight  
Distribution (MWD) for Natural Rubbers

Genus-species	Family <sup>a</sup>	Common Name	$\bar{M}_w \times 10^{-3}$	MWD ( $\bar{M}_w/\bar{M}_n$ )
<u>Hevea brasiliensis</u> Mull. arg.	EUP	Rubber tree	1310	5.2
<u>Parthenium argentatum</u> A. Gray	COM	Guayule	1280	6.1
<u>Pycnanthemum incanum</u> (L.) Michx. <sup>b</sup>	LAB	Mountain mint	495	4.0
<u>Lamiasrum galeobdolon</u> (L.) Ehrend. and Polatsch.	LAB	Yellow archangel	423	4.5
<u>Monarda fistulosa</u> L.	LAB	Wild bergamont	419	3.1
<u>Vernonia fasciculata</u> Michx.	COM	Iron weed	417	3.7
<u>Symphoricarpos orbiculatus</u> Moench	CAP	Coral berry	367	6.1
<u>Sonchus arvensis</u> L.	COM	Sow thistle	333	2.7
<u>Xylococcus bicolor</u> Nutt.	ERI	Two-color woodberry	333	2.8
<u>Melissa officinalis</u> L.	LAB	Balm	316	4.2
<u>Lonicera tatarica</u> L.	CAP	Tartarian honeysuckle	248	3.8
<u>Silphium integrifolium</u> Michx.	COM	Rosinweed	283	3.1
<u>Helianthus hirsutus</u> Raf.	COM	Hirsute sunflower	279	3.1
<u>Cirsium vulgare</u> (Savy) Ten.	COM	Bull thistle	266	3.1
<u>Cacalia atriplicifolia</u> L. <sup>b</sup>	COM	Pale Indian plantain	265	4.0
<u>Euphorbia glyptosperma</u> Engelm.	EUP	Ridgeseed Euphorbia	264	2.7
<u>Monarda didyma</u> L.	LAB	Oswego tea	263	3.2
<u>Triosteum perfoliatum</u> L.	CAP	Tinker's weed	240	3.8
<u>Solidago altissima</u> L.	COM	Tall goldenrod	239	3.0
<u>Cirsium discolor</u> (Muhl.) Spreng.	COM	Field thistle	238	3.1
<u>Solidago graminifolia</u> (L.) Salisb.	COM	Grass-leaved goldenrod	231	3.4
<u>Apocynum cannabinum</u> L.	APO	Indian hemp	216	2.7
<u>Polymnia canadensis</u> L.	COM	Leafy cup	206	3.5
<u>Gnaphalium obtusifolium</u> L.	COM	Fragrant cudweed	206	2.8

continued--

TABLE 3 -- continued

Genus-species	Family <sup>a</sup>	Common Name	$M_w \times 10^{-3}$	MWD ( $\overline{M}_w/\overline{M}_n$ )
<u>Silphium terebinthinaceum</u> Jacq.	COM	Prairie dock	197	3.6
<u>Euphorbia pulcherrima</u>	EUP	Poinsettia	197	2.7
<u>Asclepias incarnata</u> L.	ASC	Swamp milkweed	185	2.4
<u>Grindelia squarrosa</u> (Pursh.) Duval	COM	Tarweed	173	2.8
<u>Vernonia altissima</u> Nutt.	COM	Ironweed	167	2.7
<u>Solidago rigida</u> L. <sup>b</sup>	COM	Stiff goldenrod	164	3.1
<u>Euphorbia corollata</u> L.	EUP	Flowering spurge	163	3.3
<u>Helianthus grosseserratus</u> Martens	COM	Sawtooth sunflower	160	3.8
<u>Elaeagnus multiflora</u> Thunb.	ELA	Cherry Elaeagnus	156	2.9
<u>Rudbeckia laciniata</u> L.	COM	Sweet coneflower	151	2.2
<u>Pycnanthemum virginianum</u> (L.) Durand & Jackson	LAB	Mountain mint	147	2.8
<u>Campsis radicans</u> (L.) Seem. exBur.	BIG	Trumpet creeper <sup>c</sup>	146	4.4
<u>Chenopodium album</u> L.	CHE	Lambsquarter	145	3.5
<u>Monarda punctata</u> L.	LAB	Horsemint	143	4.0
<u>Apocynum androsaemifolium</u> L.	APO	Spreading dogbane	140	2.9
<u>Asclepias tuberosa</u> L.	ASC	Butterfly weed	134	2.5
<u>Nepeta cataria</u> L.	LAB	Catnip	132	2.9
<u>Teucrium canadense</u> L. <sup>b</sup>	LAB	American germander	130	3.8
<u>Solidago ohioensis</u> Riddell	COM	Ohio goldenrod	127	2.4
<u>Artemisia vulgaris</u> L.	COM	Common mugwort	127	2.6
<u>Aster laevis</u> L.	COM	Smooth aster	125	2.3
<u>Asclepias syriaca</u> L.	ASC	Common milkweed	120	3.1
<u>Artemisia abrotanum</u> L.	COM	Southernwood	120	2.4
<u>Campanula americana</u> L. <sup>b</sup>	CAM	Tall bellflower	113	2.4
<u>Centaurea vochinensis</u> Bernh.	COM	Knapweed	111	2.4
<u>Physotegia virginiana</u> (L.) Benth.	LAB	Obedient plant	109	3.1

continued--

TABLE 3 -- continued

Genus-species	Family <sup>a</sup>	Common Name	$M_w \bar{X} 10^{-3}$	MWD ( $\bar{M}_w/\bar{M}_n$ )
<u>Verbena urticifolia</u> L.	VER	White vervain	109	2.2
<u>Euphorbia cyparissias</u> L.	EUP	Cypress spurge	107	1.8
<u>Ocimum basilicum</u> L.	LAB	Purple basil	107	3.3
<u>Asclepias hirtella</u> (Pennell) Woodson	ASC	Milkweed	102	2.2
<u>Achillea millefolium</u> L.	COM	Yarrow	98	2.3
<u>Phyla lanceolata</u> (Michx) Greene	VER	Frog fruit	97.2	2.2
<u>Gaura biennis</u> L.	ONA	Gaura	93	2.4

<sup>a</sup> Code, family: APO, Apocynaceae; ASC, Asclepiadaceae; BIG, Bignoniaceae; CAM, Campanulaceae; CAP, Caprifoliaceae; CHE, Chenopodiaceae; COM, Compositae, ELA, Elaeagnaceae; ERI, Ericaceae; EUP, Euphorbiaceae; GRA, Gramineae; LAB, Labiateae; ONA, Onagraceae; VER, Verbenaceae.

<sup>b</sup> Previously selected as a promising source of natural rubber on the basis of botanical characteristic and yield of rubber and hydrocarbons.

TABLE 4  
Grass Gutta Polymers

Plant source	Month/day collected	Content of hydrocarbon polymer, %	Weight-average molecular weight $\bar{M}_w \times 10^{-3}$	Molecular weight distribution, $(\bar{M}_w/\bar{M}_n)$	$C^{13}NMR$ , characterization
<u>Agropyron repens</u>	8/11/77	1.72	111	2.4	<u>trans</u> -1,4-polyisoprene
<u>Elymus canadensis</u>	7/28/77	1.28	116	2.4	<u>trans</u> -1,4-polyisoprene
<u>Elymus canadensis</u>	9/28/77	1.48	176	2.8	<u>trans</u> -1,4-polyisoprene
<u>Elymus canadensis</u> <sup>a</sup>	10/4/78	1.86	144	2.6	---
<u>Leersia oryzoides</u>	6/29/77	0.63	---	---	---
<u>Leersia virginica</u>	9/1/77	0.67	123	2.7	<u>trans</u> -1,4-polyisoprene
<u>Phalaris canariensis</u>	9/1/77	1.15	76.8	2.7	<u>trans</u> -1,4-polyisoprene
<u>Phalaris canariensis</u>	9/28/77	1.22	123	3.5	<u>trans</u> -1,4-polyisoprene

<sup>a</sup> Average values from 30 cultivated plots harvested before maturity (seeded late)..  
Standard deviations in these measurements were respectively 0.40% gutta content, 16  $\bar{M}_w$ , 0.4  $\bar{M}_w/\bar{M}_n$ .

polymers and gutta is distinguished from rubber chiefly in that it readily crystallizes upon standing at room temperature<sup>2,3,6</sup> (Figure 7). However, this procedure would not readily distinguish between mixed cis-trans-1,4-polyisoprenes and the pure cis polymers. When the polyisoprene content is high enough to merit further characterization, nuclear magnetic resonance (NMR) is used to determine detailed chemical structure; but so far mixed isomers have not been identified.

The older traditional methods of detecting rubber in plant extractives could scarcely distinguish between rubber and gutta.<sup>16</sup> Thus, it is possible that there are species producing mixed cis-trans-polyisoprenes. However, such details of structure are immaterial from a practical viewpoint for low-molecular weight polyisoprenes considered only as a hydrocarbon source.

#### LIGNOCELLULOSE CONVERSION PRODUCTS

Since considerable research is in progress and several recent symposiums and reviews have been given on biomass conversion to fuels and feedstocks, we have limited our discussion of this subject to the extractive-free residues from botanocemical processing of potential new crops. These residues would be the main product by weight of a botanocemical extraction process and would be available as "flakes" for subsequent chemical or microbiological conversion to a wide variety of secondary botanocemical (Figure 8).

The minimum value for extractive-free residue would be about \$50/ton (July 1979) as a solid fuel. There are several thermal-pyrolytic-catalytic routes to gaseous and liquid fuels or petroleum substitutes from lignocellulose.<sup>1,11,13,14,18</sup> Anaerobic fermentation is another alternative route to gaseous fuel, i.e., methane.

Extractive-free residues would be especially attractive sources of lignocellulose for saccharification to sugars for fermentation to fuel alcohol, as suggested also in Figure 1. Pentosans in the residue can either be converted to 5-carbon sugars for fermentation or to furfural.

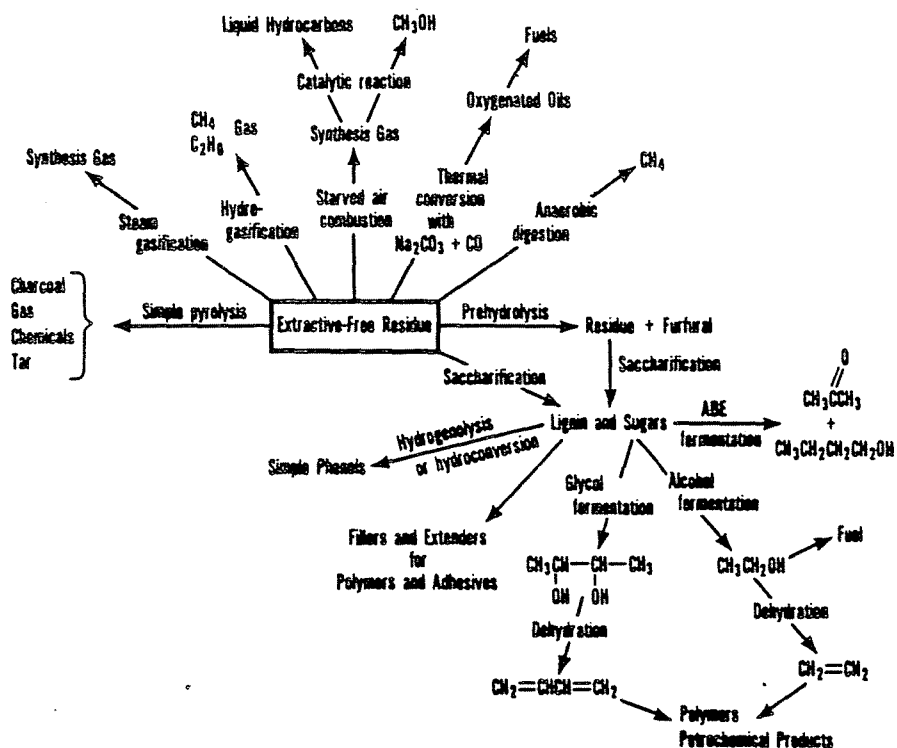


Fig. 8 Conversion of extractive-free lignocellulosic residues to botanochemicals.

Other secondary botanochemicals that could be produced economically by fermentation of low-cost sugars include acetone, butanol, and 2,3-butanediol. Alternately, many of these residues could be used for nonbotanochemical applications. The process for flaking whole-plant produce can be conducted with minimum damage to the fiber so that the residue can be used for paper- or board-making. Also, any of several treatments for increasing the digestibility and the protein content of the residues would yield a valuable cattle feed.

## CONCLUSION

Green plants are solar-powered chemical factories which convert CO<sub>2</sub> and H<sub>2</sub>O to an immense variety of energy-rich organic compounds. As green plants grow, they efficiently store energy and materials. Crops can be developed to help meet the need for renewable sources of fuels and feedstocks, and conceptually botanochemical production systems are economically feasible. Thus, phytochemical research is now perceived as highly relevant, even urgent. Moreover, a developing opportunity exists for phytochemists to contribute to the creation of new crops, new industrial processing systems, and a new green-crop-based synthetic botanochemical industry.

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